Chromium Oxidation States

- Oxidation states range from +2 to +6.

- We will see +6, +3, and +2

Oxidation state	+6	+3	+2
Ions	$CrO_4^{2-}/Cr_2O_7^{2-}$	$Cr^{3+}(aq)$	$Cr^{2+}(aq)$
Color	orange/red-orange	green	blue-violet
Configuration	$3d^0$	$3d^3$	$3d^4$
Magnetism	diamagnetic	paramagnetic	paramagnetic

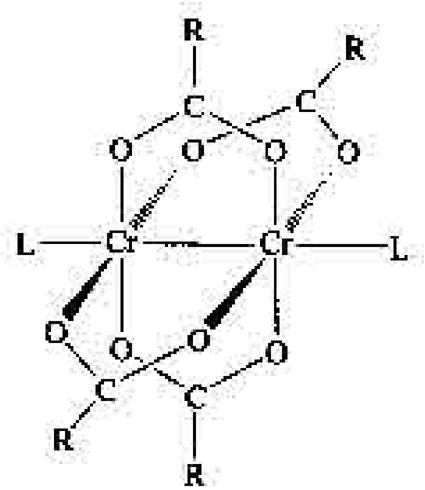
Chromium(II) Acetate Dihydrate
$Cr_2(O_2CCH_3)_4(H_2O)_2$

- Discovered in 1844

- Unusual for Cr(II)
  - Brick red
  - Diamagnetic

- One of a family of compounds $Cr_2(O_2CR)_4L_2$

- All have short Cr–Cr distances (228 to ~254 pm) due to quadruple bonds.



- Cr–Cr quadruple bonding accounts for diamagnetism and atypical color.

Chromate and Dichromate Ions

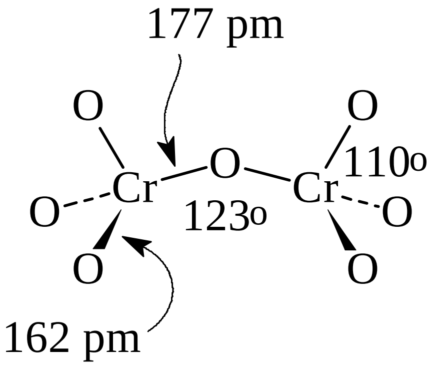
✔ Potassium dichromate, $K_2Cr_2O_7$, is the starting material for this synthesis.

- In alkaline or basic solution, chromium(VI) exists as the orange-colored tetrahedral CrO_4^{2-} ion

- In acid solution, this can become $HCrO_4^-$, but dimerization to red-orange $Cr_2O_7^{2-}$ predominates:

$$H_2CrO_4 + H_2O \rightleftharpoons HCrO_4^- + H_3O^+ \qquad K_1 = 4.1$$
$$HCrO_4^- + H_2O \rightleftharpoons CrO_4^{2-} + H_3O^+ \qquad K_2 = 1.3 \times 10^{-6}$$
$$2\,CrO_4^{2-} + 2\,H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O \qquad K = 6.3 \times 10^{-3}$$

- Dichromate ion has two tetrahedrally coordinated Cr atoms linked by an oxygen bridge:



- Intense colors of CrO_4^{2-} and $Cr_2O_7^{2-}$ are the result of ligand-to-metal (L→M) charge transfer bands,

$$Cr^{6+}\text{–}O^{2-} \rightarrow Cr^{5+}\text{–}O^-$$

Synthesis Redox

✔ In this synthesis we will reduce Cr(VI) to Cr(III) and then to Cr(II).

- Dichromate is a strong oxidizing agent:

$Cr_2O_7^{2-} + 14\ H^+ + 6\ e^- \rightleftharpoons 2\ Cr^{3+} + 7\ H_2O \qquad E^o = +1.33\ \text{V}$

- Cr(III) is a weak oxidizing agent, which requires a strong reducing agent to produce Cr(II):

$Cr^{3+} + e^- \rightleftharpoons Cr^{2+} \qquad E^o = -0.41\ \text{V}$

- In this synthesis, zinc metal serves as the strong reducing agent:

$Zn \rightleftharpoons Zn^{2+} + 2\ e^- \qquad -E^o = +0.763\ \text{V}$

Overall Redox Equation

✔ Actual overall reaction in this synthesis is not certain.

- From the electrode potentials, it might be assumed that the reduction of Cr(VI) to Cr(II) is accomplished by Zn as the reducing agent, in which case the balanced equation would be

$$Cr_2O_7^{2-} + 14\ H^+ + 4\ Zn \rightarrow 2\ Cr^{2+} + 4\ Zn^{2+} + 7\ H_2O$$

- But in this preparation, Zn and H^+ from the acid are reacting to produce $H_2(g)$:

$$2\ H^+ + Zn \rightarrow H_2 + Zn^{2+}$$

- Hydrogen gas might be the reducing agent for converting Cr(VI) to Cr(III). If so, the reduction of Cr(III) to Cr(II) would then be effected by Zn as the reducing agent in a second step.

$$\begin{array}{rcl} Cr_2O_7^{2-} + 3\ H_2 + 8\ H^+ & \rightarrow & 2\ Cr^{3+} + 7\ H_2O \\ 2\ Cr^{3+} + Zn & \rightarrow & 2\ Cr^{2+} + Zn^{2+} \\ \hline Cr_2O_7^{2-} + 3\ H_2 + 8\ H^+ + Zn & \rightarrow & 2\ Cr^{2+} + Zn^{2+} + 7\ H_2O \end{array}$$

- More likely, the first step is a mixture of reduction by H_2 and reduction by Zn.

☞ Regardless of the exact stoichiometry, the limiting reagent is $Cr_2O_7^{2-}$, from which twice as many moles of Cr^{2+} is produced.

$Cr^{2+}(aq)$ to $Cr_2(O_2CCH_3)_4(H_2O)_2$

- Color of the original dichromate solution changes from red-orange to green and then to blue.

- When the solution is blue, conversion to Cr^{2+} is complete.

- At this point, using the pressure from the evolving $H_2(g)$, the solution is pumped into a solution of sodium acetate, where the complex forms and is precipitated as a brick-red solid:

$$2\,Cr^{2+} + 4\,CH_3CO_2^{-} + 2\,H_2O \rightarrow Cr_2(O_2CCH_3)_4(H_2O)_2$$

☞ When wet, the complex is subject to oxidation to Cr(III) from oxygen:

$$\begin{array}{rcll} Cr^{2+} & \rightarrow & Cr^{3+} + e^{-} & -E^{o} = +0.41\text{ V} \\ O_2 + 4\,H^{+} + 4\,e^{-} & \rightarrow & 2\,H_2O & E^{o} = +1.229\text{ V} \end{array}$$

☛ Avoid sucking air through the wet product during the cold-water and alcohol washes.

☛ After the final ether wash, allow air to pass through the product on the filter for about 30 sec., then collect it on a large piece of dry filter paper or a porcelain plate to allow the residual ether to evaporate.